

Separation and recovery of rare earth elements from spent nickel–metal-hydride batteries using synthetic adsorbent

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ABSTRACT

The recovery of rare earth elements such as La(III) and Nd(III) from spent nickel–metal hydride (NiMH) battery by novel synthetic adsorbent were investigated. First, layered double hydroxide (LDH)-A (A^- anion of carrier) been prepared and characterized by different methods. Second, the separation and recovery of some rare earth elements (La(III) and Nd(III)) from acidic solutions using the synthetic adsorbent were investigated. The adsorption percent of the two metal ions was found to increase with increasing contact time, adsorbent weight and pH from 0 to 1 then it remains constant in the pH range (1–2). La(III) was preferentially adsorbed over Nd(III) in the mixture solution. From characterization of the adsorbent results, the adsorption mechanism of LDH-A adsorbent was proposed with rare earth elements. It was found that the highest separation factor ($S_{La/Nd}$) value of 23.2 was obtained with 10 g/l (0.1 g/10 ml) from a mixed solution of 5 g/l of each of La(III) and 5 g of Nd(III) at pH 1 and contact time 2 h. Based on the experimental results, a separation method was developed and tested to separate high purity Co(II), Ni(II) and rare earths from Ni-MH batteries leached by 2.0 M H_2SO_4 and the rare earths are leached by 2 M HCl. Based on the experimental results, a flow sheet was developed and tested and 1.2 g La(III) and 1 g Nd(III) were obtained from the leaching process.

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1. Introduction

Rechargeable, high-powered nickel metal hydride (NiMH) batteries are widely used as power sources for cell phones, digital cameras, hybrid cars and so on. On the other hand, a large quantity of these battery wastes discharged from their production factories and from spent NiMH batteries have been disposed off as waste even though they contain valuable transition and rare earth elements. The amount of both wastes is hundreds of tons per year in Egypt. The establishment of a method of recovering these elements from the waste in an environmentally thoughtful way is therefore desirable. The recovery of these elements from spent NiMH batteries has been previously examined by extraction with organic solvents, magnetic separation and electrochemical deposition (Li et al., 2009; Tenorio and Espinosa, 2002; Tzanetakis and Scott, 2004a,b). In the last few years there is a marked decrease in the amounts of these valuable elements in the international market. Therefore, there is a great need for development of other sources of rare earths and new processes that reduce the cost of rare earths separations.

Layered double hydroxides (LDHs), also known as hydrotalcite (HT)-like materials, are a class of synthetic two-dimensional nano-structured anionic clays. The structure of these materials can be described as containing brucite-like layers; a fraction of the divalent

cations coordinated octahedrally by hydroxyl groups which have been replaced isomorphously by trivalent cations, giving positively charged layers with charge- balancing anions between them. Some hydrogen bonded water molecules may occupy any remaining free space in the interlayer region (Cavani et al., 1991; Crepaldi and Valim, 1998). LDHs may be represented by the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} ($M = Mg, Fe, Co, Cu, Ni, \text{ or } Zn$) and M^{3+} ($M = Al, Cr, Ga, Mn \text{ or } Fe$) are di- and trivalent cations, respectively; the value of x is equal to the molar ratio of $M^{2+}/(M^{2+} + M^{3+})$ and is generally in the range 0.2–0.33; A^{n-} is an anion. LDHs, both as directly prepared or after thermal treatment, are promising materials for a large number of practical applications in catalysis, adsorption, pharmaceuticals, photochemistry, electrochemistry and other areas (Gasser et al., 2008; Gasser and Aly, 2009; Zhou, 2010; Gasser, 2009). This is due to their high versatility, their easy tailored properties and low cost, which make it possible to produce materials designed to fulfill specific requirements. The anionic exchange capability of LDHs can be utilized to good advantage by intercalating large organic anions, such as carrier, in the interlayers. Accessibility of the interlayer region of the resulting so-called organo-LDHs enhanced sorption capacity for a diverse range of organic pollutants and inorganic materials (cations).

In this context, the present work aims to recover rare earth elements from spent NiMH batteries and utilization of recovered metals for conservation of resources and for environmental protection. The applied technique is considered as environmentally friendly with no hazardous by-products. The cost of the recovered products by the

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studied process is expected to be competitive with the market price for the same chemicals prepared from primary resources. The utilization of LDH prepared using separate nucleation and aging method and their derivatives for recycling of a Nickel Metal Hydride batteries (NiMH battery) which contain rare earth elements is investigated. In this study, batch type experiments were conducted to investigate the capacity and uptake of REEs by Mg–Fe–LDH-A. The effects of some parameters, such as contact time, system pH, and adsorbent weight were investigated. This process was tested to separate La(III) and Nd(III) from NiMH batteries leached by H_2SO_4 .

2. Experimental

Experiments were done by using both real and simulated solutions containing 5 g/l REE salts only for investigating the uptake of REEs on the prepared adsorbent.

2.1. Major reagents and materials

Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid), HA, was kindly offered by Cyanamid Canada and used as carrier in this application has been published (Rickelton et al., 1997).

All the chemicals used were of analytical reagent grade (AR) and obtained from The British Drug Houses (BDH), England.

NiMH batteries (50% cylindrical and 50% prismatic batteries) from one manufacturer (Nokia) were used in this study. Plastic and metallic cases were firstly removed according to the manual procedure depicted elsewhere.

2.2. Adsorbent synthesis

The synthesis of MgFe-LDH-A includes two steps: the preparation of (MgFe-LDH- CO_3) and the anion-exchange reaction of this compound with the anion (A^-) of Cyanex 272 (HA) as carrier, to obtain MgFe-LDH-A.

A reddish-brown solution of $MgCl_2 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ with Mg/Fe ratio of 4 was added to a vigorously stirred solution of NaOH and Na_2CO_3 with separate nucleation and aging steps (Zhao et al., 2002). The resulting reddish-brown suspension was aged at 100 °C for 12 h. The mixture was filtered and the solid obtained after washed thoroughly with deionized water and dried at 80 °C for 24 h affording a pale yellow solid.

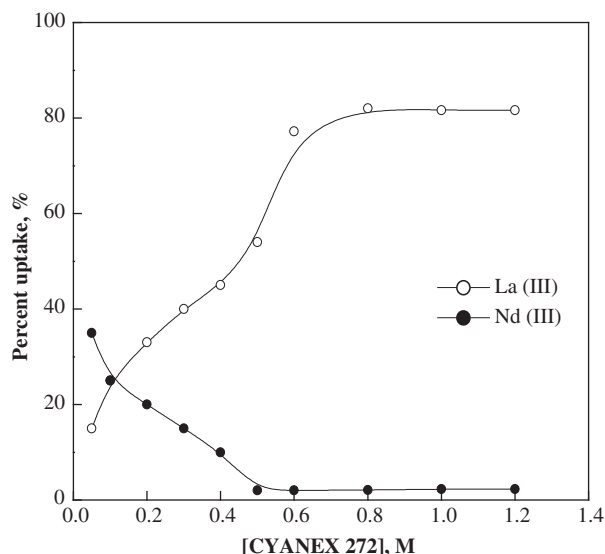


Fig. 1. Effect of carrier concentration embedded in the LDH host on the adsorption of 5 g/l La (III) and Nd (III) using 0.1 g adsorbent/10 ml solution at pH = 1.

Table 1

Effect of Mg(II)/Fe(III) ratio.

La(III) = 5 g/l, pH = 1.

Adsorbent weight = 0.1 g, solution volume = 10 ml, temperature = 25 °C.

Mg(II)/Fe(III) ratio	Uptake, %	Concentration of La(III) recovered (mg/g)
2:1	62.0	310
3:1	75.0	375
4:1	84.0	420

A finely-ground sample of Mg–Fe–Cl LDH (1 g) was dispersed in a solution of Cyanex 272 (0.05–1 M) in kerosene (100 ml) and stirred while heating at 25 °C for 1 h. The resulting solid was separated by filtration, washed well with deionized water and dried at 50 °C. A pale yellow solid (adsorbent) was obtained.

2.3. Characterization of the adsorbent

The characterization of the adsorbent by XRD and FT-IR spectra was investigated. X-ray diffraction (XRD) patterns were obtained at 20 mA, 40 kV with Philips PW 3710 powder diffractometer equipped with Ni-filtered $Cu K_{\alpha}$ radiation. Infrared spectra were obtained with a Bruker IFS-88 FT-IR spectrometer by a standard KBr disk method.

2.4. Uptake experiments

In the uptake process, the aqueous phase (10 ml) containing 5 g/l of each La(III) and Nd(III) was shaking with 0.1 g weight of adsorbent of different concentrations of carrier. The La(III) and Nd(III) concentration were analyzed and determined by atomic absorption spectrometry (AAS), Model (S4) thermo Electron Corporation. The optimum initial pH, contact time and concentration of metal salts for the metal intercalation Mg–Fe-LDH-carrier were investigated. For studying the effect of pH, the initial pH of the solutions was adjusted by HCl or NaOH to the desired value. The samples were equilibrated for 2 h, unless otherwise stated. All the uptake experiments were carried out at ambient temperature 25 ± 1 °C.

The distribution coefficient (K_d ml/g) of metal ions between the aqueous phase and the solid phase was calculated from Eq. (1)

$$K_d = (C_o - C_e) / C_e \times V / m \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations (mg/l) of metal ion in solution, V is the volume (L) and m the weight (g) of the adsorbent.

The separation feasibility of La(III) from Nd(III) was evaluated in terms of the separation factor, $S_{(La/Nd)}$, and defined by the following Eq. (2);

$$S_{(La/Nd)} = K_{d(La)} / K_{d(Nd)} \quad (2)$$

2.5. Regeneration of used adsorbent

In the present study, used Mg–Fe-LDH-A was regenerated using 0.01 M HCl. The efficiency for REEs uptake by the regenerated adsorbent after several uptakes was also investigated. After completing equilibrium uptake experiments, the suspensions were recovered using 0.01 M HCl and the recovered adsorbent was reused to uptake REEs. This procedure was repeated several times and the amount of REEs uptake after each cycle was determined.

2.6. Isotherms study

All batch adsorption experiments were performed in centrifuge tubes at room temperature and contained 0.1 g of LDH-A and 10 ml

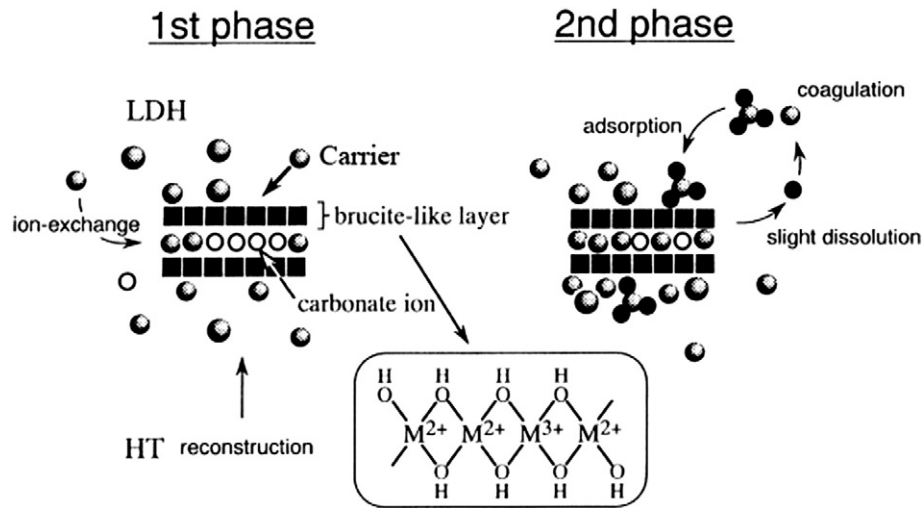


Fig. 2. Schematic diagram of adsorption mechanism.

of La(III) solution (5–10 g/l). The solutions were brought to pH 1. The tubes were shaken at room temperature for 2 h. The amount of metal ion retained in the adsorbent phase, q_e (mg/g), was calculated using Eq. (3):

$$q_e = (C_0 - C_e) V/m. \quad (3)$$

The adsorbed La(III) concentration was calculated as the difference in the La(III) concentration before and after adsorption and was expressed as mg/g dry LDH.

2.7. Recovery of La(III) and Nd(III) from spent Ni–MH batteries leach solution

The internal content of batteries (including the grids that support the active material) was weighed, dried in a drying oven for 24 h at 60 °C, and weighed again to measure the content of volatile substances. One battery was randomly chosen and was subjected to qualitative metal characterization using Energy Dispersive Spectrometer in order to identify the main metal species present in the NiMH batteries as well as qualitative metal composition. The real solution was obtained by leaching electrode materials of prismatic cells of NiMH spent batteries. The cells were cut in half longitudinally to extract the internal materials (electrodes plus a nylon separator) from

the metallic cases. Both positive and negative electrodes were mechanically crumbled and then were leached using a 2 M sulfuric acid solution at solid/liquid ratio of 1/10, under agitation for 2 h at 25 °C. After leaching, the leach solution and the reminder residue were separated by filtrations. REE sulfate in filtrate was precipitated using NaOH at pH = 2.5. Analyses for cobalt nickel content were determined in the leach solution by atomic absorption. The resulting liquor solution was a dark green solution of pH about 2.4. After leaching, the insoluble residue (white dense ppt $RE(OH)_3$) was leached by 2 M HCl for Recovery of $LaCl_3$ and $NdCl_3$. The resulting liquor was determined by atomic absorption spectrometry (AAS).

The adsorption process which applied on the leaching solution that contains both La(III) and Nd(III) was carried out by LDH-A adsorbent.

3. Results and discussion

3.1. Factors affecting in the uptake of La(III) and Nd(III)

There are different factors affecting in the uptake of La(III) and Nd(III). Some of these factors concerning with the synthesis of the adsorbent such as carrier concentration and changing the M(II)/M(III) ratio. The others concerning with the adsorbate such as contact time, adsorbent weight and pH.

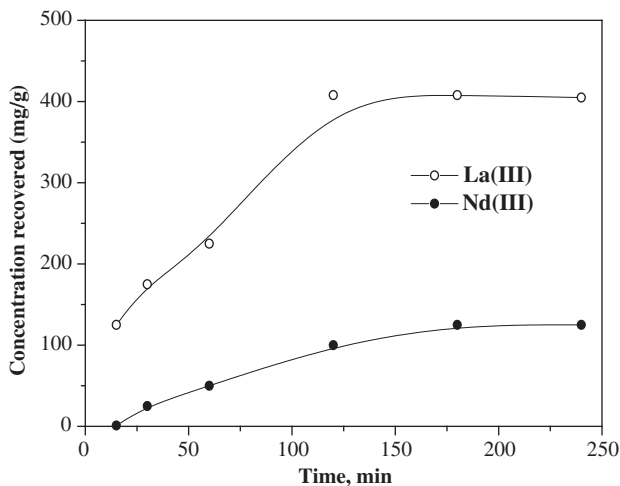


Fig. 3. Effect of contact time on the uptake of La(III) and Nd(III). La(III) = 5 g/l Nd(III) = 5 g/l. pH = 1 adsorbent weight = 0.1 g/10 ml. Temperature = 25 °C.

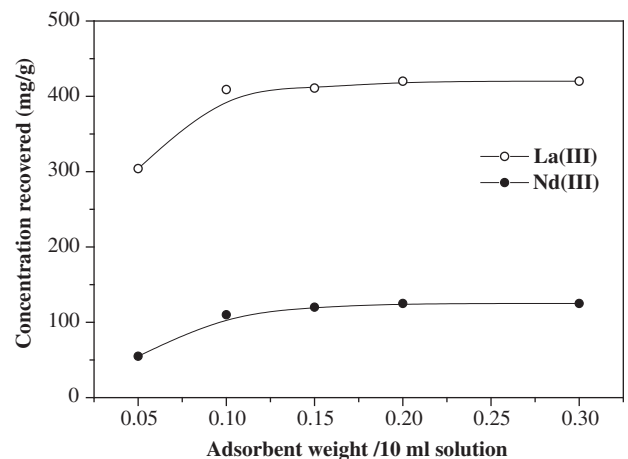


Fig. 4. Effect of adsorbent weight on the uptake of La(III) and Nd(III). La(III) = 5 g/l, Nd(III) = 5 g/l. Contact time = 2 h, pH = 1. Temperature = 25 °C.

Table 2

Effect of pH.

La(III) = 5 g/l, Nd(III) = 5 g/l.

Adsorbent = 0.1 g/10 ml, temperature = 25 °C.

pH	Uptake, %		Concentration recovered (mg/g)	
	La (III)	Nd(III)	La (III)	Nd(III)
0.0	57.5	20	288	100
1.0	81.4	22	409	110
2.0	81.0	20	405	100

3.1.1. Factors concerning with the synthesis of adsorbent

The effect of carrier (Cyanex 272) concentration embedded in the LDH host was investigated to prepare Mg-Fe-LDH-A (adsorbent). The uptake percent of La(III) increases with the increase in the carrier concentration in the prepared adsorbent till 0.6 M after which the uptake remains constant till 1.2 M. Meanwhile, the uptake percent of Nd(III) decreases with increase in the carrier concentration till 0.5 M after which it remains constant, Fig. 1. Therefore the adsorbent was prepared using 0.6 M carrier. The difference between the adsorption behavior of Nd (III) and La (III) can be explained by differences in ionic radii ($\text{Nd}^{3+} = 1.821 \text{ \AA}$ and $\text{La}^{3+} = 1.877 \text{ \AA}$). The steady decrease in the atomic and ionic radii with the increase in the atomic number of lanthanide ions is known as lanthanide contraction. Since the covalent character of hydroxides of lanthanides increases as the size decreases from La(III) to Lu(III), which leads to the decreases in basic strength, therefore, basicity of lanthanides decreases from La^{3+} to Nd^{3+} .

The effect of changing the Mg(II)/Fe(III) ratio in the preparation of LDH-carrier was studied. The uptake of La(III) increased with increasing the Mg/Fe ratio in the range 2 to 4, Table 1. The results of these experiments proved that the uptake of La(III) is reached maximum after reaching the Mg(II) to Fe(III) ratio 4 in the three investigated systems. The anion adsorption of carrier (Cyanex272) onto the LDHs and HT compounds occurred by two phases (Fig. 2.) (Seida et al., 2000). In the first phase, the adsorption occurred rapidly. In the HT compounds, the reconstruction of LDH structure occurs simultaneously accompanied with the adsorption of carrier substances in the first phase. In the second phase, the small amount of hydroxides produced by a slight dissolution of the compounds promoted the coagulation of carrier substances onto the compounds. The hydroxide-induced coagulates adsorbed onto the

Table 3

Supplementary XRD data for MgFe-A and reference LDHs.

	MgFe-A	Mg-Fe-CO ₃
$d_{003} (\text{\AA}^\circ)$	21.38	7.81
$2\theta (^\circ)$	4.1	11.32
$d_{006} (\text{\AA}^\circ)$	7.31	3.90
$2\theta (^\circ)$	12.10	22.81
$d_{009} (\text{\AA}^\circ)$	4.86	2.62
$2\theta (^\circ)$	18.22	34.19
$d_{110} (\text{\AA}^\circ)$	1.52	1.52
$2\theta (^\circ)$	60.86	60.77

compounds resulting in sludge with very low water content. The slow ion exchange between carbonate ions in the compounds and carrier substances would also occur in the second phase. Fig. 2 shows the amount of adsorption for series of compounds and their HT ones. The amount of adsorption increased with increasing the M(II)/M(III) ratio. Although the M(III) ions in the brucite-like layer produce the anion exchange site, the amount of adsorption increased with decreasing the content of M(III) ion in the compounds. The results of adsorption in Table 1 implies the adsorption of carrier substances at the hydroxyl groups of M(II) as well as at the inner layer anion exchange site. The surface hydroxyl groups of the compounds would work as coagulation sites. The carrier substances with a large molecular size should be adsorbed onto the surface of the LDHs and not intercalate in the inner layer of the LDHs due to the larger size of them. The HT compounds show a larger adsorption capacity especially in lower concentration region as shown in Table 1. The study of intercalation of anionic surfactants into surfactants into the LDH inner layer (Seida et al., 1998), the HT-compounds are able to intercalate a large amount and a larger size of guest molecules during their reconstruction of layered structure compared to the LDHs.

3.1.2. Factors concerning with the adsorbate

The effect of contact time on the uptake of 5 g/l of La(III) and Nd(III) are shown in Fig. 3. As the contact time increases the uptake of La(III) increases gradually until the uptake remains constant with any further increase in the contact time at 2 h. While the uptake of Nd(III) is slightly increase. The difference between the adsorption behavior of Nd (III) and La (III) was mentioned before.

The effect of adsorbent weight on the uptake of La(III) and Nd(III) was studied in the range of 0.05–0.3 g. It was observed that the uptake of La(III) increase by increasing the weight of adsorbent from

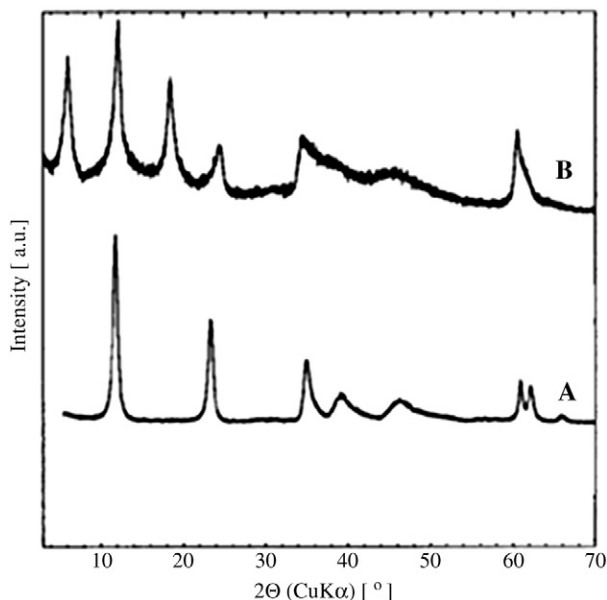


Fig. 5. X-ray powder diffraction patterns of Mg-Fe double hydroxides: (A) MgFe-CO₃-LDH and (B) MgFe-ALDH.

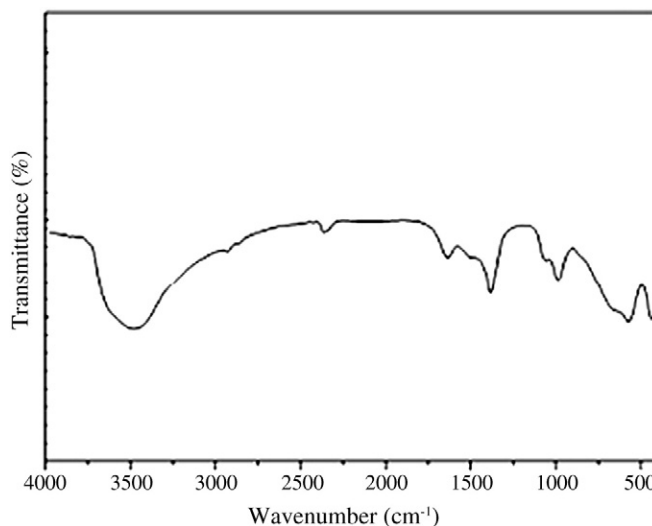


Fig. 6. FT-IR for spectra Mg-Fe(III)-CO₃ LDH prepared by separate nucleation and aging method with Mg(II)/M(III) = 4.

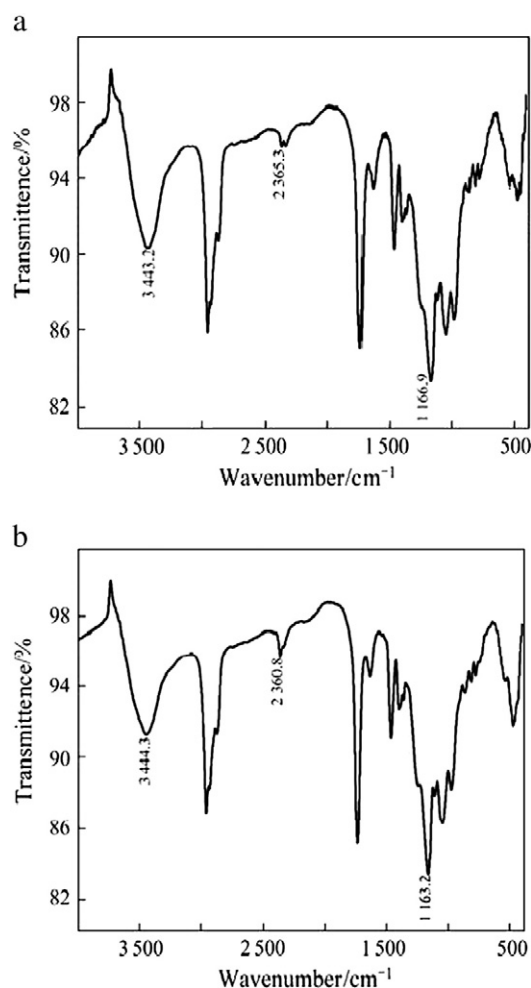


Fig. 7. FT-IR spectra of MgFe-LDH-Cyanex272 before (a) and after (b) adsorption rare earths.

0.05 g to 0.1 g, until a constant value is reached at 0.2 g, while there is slightly increase in the case of Nd(III), Fig. 4.

The effect of pH, while keeping all other experimental conditions fixed as mentioned in the experimental section, was investigated in the range (0–2). It was found that the uptake of La(III) increases with increases of pH from 0 to 1 then the uptake remains constant in the pH range (1–2), Table 2.

3.2. Characterization of MgFe-CO₃ LDH and MgFe-A LDH

The results of powder XRD measurements are shown in Fig. 5. It can be readily seen that the pattern B of MgFe-A has a specific set of reflection peaks that significantly differs from those of reference materials (the pattern A). The three symmetric peaks at 2θ at 4.1, 12.10 and 18.22° revealed

Table 4

Effect of metal ions concentration on separation factor of La(III) and Nd(III) by synthetic adsorbent, time: 2 h, Adsorbent weight = 0.1 g, solution volume = 10 ml, temp.: 25 °C.

Concentration of each La(III) and Nd(III), g/l	Separation factor, $S_{(La/Nd)}$
5	23.2
6	13.5
7	11.4
8	9.3
9	8.6
10	6.3

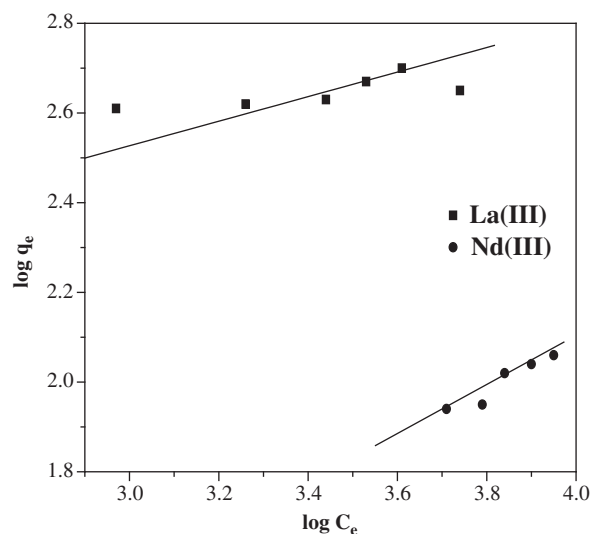


Fig. 8. Freundlich plot for the adsorption La(III) and Nd(III) and by prepared adsorbent pH 1, contact time 2 h and temperature 25 °C.

basal spacing d of 21.4, 7.3 and 4.9 Å°. These results indicated that the newly synthesized double hydroxide phase had a layered structure (Table 3). Furthermore, the subtraction of 4.8 Å° as an average brucite sheet thickness from the d value gave 16.6 Å° for the interlayer distance that can be attributed to intercalation of the A[−] chelate. Further, the fact that the two LDH samples showed reflection peaks near 2θ 60° and therefore the same d_{110} value (1.52 Å°) indicated that no change in the average cation–cation distance in the brucite-like layers had occurred.

A further support for the formation of Mg–Fe LDH intercalated with carrier anion, A[−], diffuse reflectance FTIR spectroscopy was applied. The FT-IR spectra of Mg–Fe(III)–CO₃ LDHs are shown in Fig. 6. The bands below 550 cm^{−1} are M–O vibration modes (Meng et al., 2004) and the pattern in this area is very similar for the two LDH under study, Figs. 6 and 7. The spectrum of MgFe(III)–CO₃ LDH shows an intense band at around 1370 cm^{−1} associated with the carbonate ion. This band disappeared in the new spectrum of the carrier anion chelated LDH with the appearance of sharp band at 1166.9 cm^{−1} corresponding to PO characteristic vibration band of the carrier, Figs. 6 and 7a. This indicates that anion exchange had occurred and the cyanex272 carrier intercalated into MgFe-LDH to form the adsorbent MgFe-A-LDH.

Further, Fig. 7 shows the IR spectra of MgFe-LDH-A before and after extracting La(III). Comparing the spectra in Fig. 7(a) and (b), a slight shift of O–H stretching vibration from 2365.3 cm^{−1} in Fig. 7(a) to 2360.8 cm^{−1} in Fig. 7(b). In addition, P=O band in MgFe-LDH-A was slightly shifted from 1167 to 1163 cm^{−1} after metal uptake. These indicate that the metal ions are taken as a result of extraction with the active site of the carrier. When this carrier adsorb rare earth, the O–H bonds break to form O–RE bonds, and RE³⁺ bonds with the lone-pair electron in P=O ligand.

3.3. Separation and recovery of rare earth mixture study

The separation factor, $S_{(La/Nd)}$ for the adsorbent was studied in the range of each metal ions concentration (La(III) and Nd(III)) 5 g–10 g. As shown in Table 4, the separation factor, $S_{(La/Nd)}$, decreases for with

Table 5

Freundlich parameters for adsorption of La(III) and Nd(III) onto prepared adsorbent.

Metal ion	k	n	r ²
La(III)	218.8	11.1	0.734
Nd(III)	1.41	2.1	0.963

r² is the correlation coefficient.

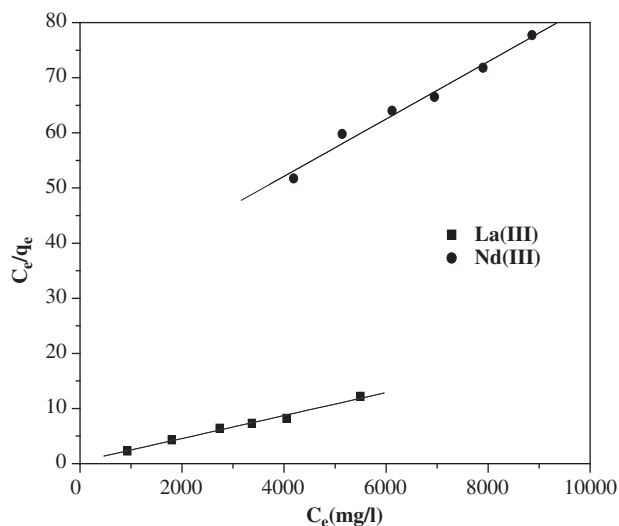


Fig. 9. Langmuir plot for the adsorption La(III) and Nd(III) and by prepared adsorbent pH 1, contact time 2 h and temperature 25 °C.

the increase in metal ions concentration to reach a minimum value of 6.3 at the concentration 10 g and a maximum value of 23.2 at the concentration 5 g. The value of separation factor obtained for the synthetic adsorbent in the work, is higher than that reported by others in the literature for extraction of La(III) and Nd(III) from acidic solution (Zhang et al., 2009).

3.4. Isotherm study

The equilibrium adsorption experimental data obtained in this study were analyzed by the commonly used Freundlich and Langmuir isotherm models. The experimental results obtained for the adsorption of these metal ions on adsorbent at room temperature (25 ± 1 °C) under optimum conditions of contact time and weight of adsorbent was found to obey the Freundlich adsorption isotherm according to the following equation:

$$\log q_e = \log k + 1/n \log C_e \quad (4)$$

where q_e is the amount of La(III) and Nd(III) removed per unit weight of adsorbent (mg/g); C_e the concentration of La(III) and Nd(III) at equilibrium; k is a constant, which is related to adsorption capacity of LDH (mg/g) and n is a constant representing the intensity of adsorption. The plot of $\log q_e$ versus $\log C_e$ for various initial concentrations of La(III) and Nd(III) is found to be linear, Fig. 8. This indicates the applicability of the Freundlich adsorption isotherm to this adsorbate–adsorbent system. The value of n was calculated from the slopes of the straight lines and found to be 11.1 and 2.1 for La(III) and Nd(III), respectively. This result indicates that the adsorbent used is more efficient for La(III) adsorption than Nd(III). Since the values of n lie between 1 and 10, it indicates that the adsorption is favorable (Mckay et al., 1982). The values of k which are related to adsorption

Table 6
Langmuir parameters for adsorption of La(III) and Nd(III) onto prepared adsorbent.

Metal ion	Q_{\max} , mg/g	b	r^2
La(III)	480.8	5.1×10^{-3}	0.997
Nd(III)	192.3	1.7×10^{-4}	0.991

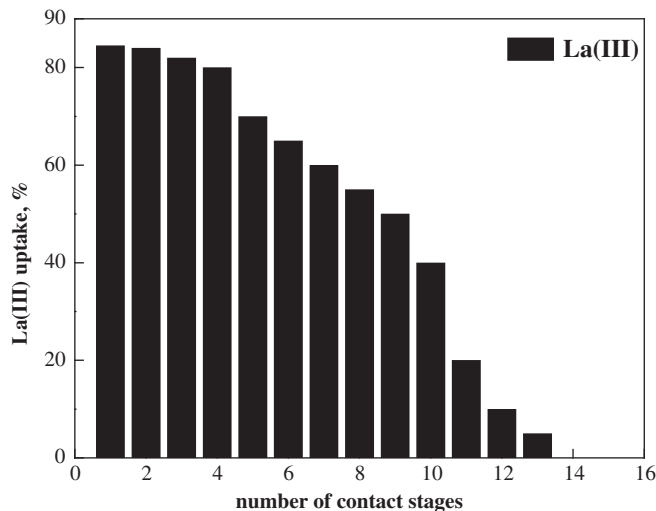


Fig. 10. Effect of regeneration of adsorbent in the adsorption of 5 g/l La (III) with 0.1 g adsorbent.

capacity are presented in Table 5. These values were calculated from the intercept of the straight lines are given in Fig. 8.

The investigated equilibrium adsorption of La(III) and Nd(III) can be mathematically expressed in terms of the adsorption isotherms. The adsorption data are commonly fitted to the Langmuir model at 25 °C. The Langmuir equation was applied to the adsorption equilibrium for LDH, using the expression,

$$(C_e/q_e) = 1/(Q_{\max}b) + C_e/Q_{\max} \quad (5)$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium (mg/g), b is Langmuir constant refer to the energy of adsorption and Q_{\max} is the adsorption capacity (amount of adsorbate adsorbed per unit mass of the adsorbent to complete monolayer coverage (mg/g)). The linear plots of C_e/q_e vs C_e show that the adsorption obeys the Langmuir model, Fig. 9. The adsorption capacity of the prepared adsorbent for La(III) and Nd(III) were 480.8 and 192.3 mg/g, respectively, Table 6.

3.5. Regeneration of used adsorbent

The performance of LDHs depends not only on the uptake but also on its stability. Although, the present adsorbent is stable enough to uptake most of La(III) (5 g/l) in the solution, it is of interest to investigate regeneration for long term operation. The regeneration of the LDHs was tested by carrying out the uptake studies repeatedly using the same Mg–Fe–carrier-LDH. It is found that the uptake percent of La(III) decreases from 87% to 60% after seven runs, Fig. 10.

Table 7
Leaching yields of spent batteries.

Element	Anode (yields %) %	Cathode (yields %) %	Anode + cathode (g/l)
Ni	76.6	100	14.00
Co	97.6	100	2.00
Fe	1.0	1	0.13
Zn	–	100	0.28
Ln	92.5	–	RE = 2.25
Nd	95.6	–	

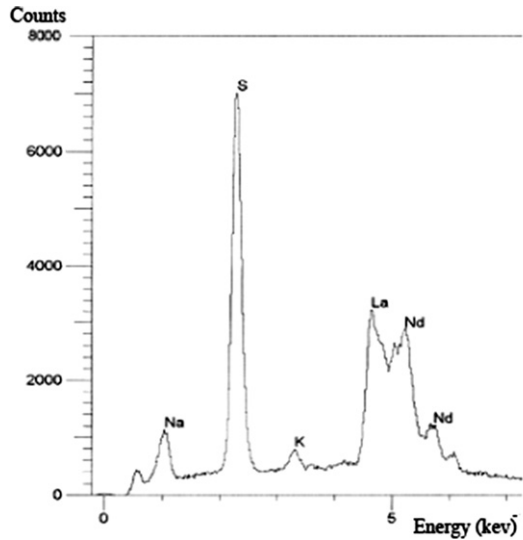


Fig. 11. Energy dispersive X-ray (EDX) spectrometer analysis of a dense white precipitate which corresponding to removal of rare earth elements.

3.6. The leaching process of NiMH battery and precipitation tests

Sulfuric acid has been chosen, after comparison with other leaching agents, considering, besides the metal yields, the economic aspects and, in particular, the low iron dissolution rate of the electrode grids (Pietrelli et al., 2002). This requirement is necessary because considering the whole batteries treatment process, iron can produce many problems during the successive selective separation steps for Ni, Co and Zn, performed by ion exchange and solvent extraction (Pietrelli et al., 2004). Leaching solutions contained 2 M of H_2SO_4 and 2.25 g/l of rare earth. The leaching efficiency for each metal is reported in Table 7. The cathode is completely dissolved ($\text{Ni}(\text{OH})_2$), while leaching of anode depends on the charge/discharge status of the electrodes, probably due to the Ni metal form (Zhang et al., 1998).

The aqueous solution used in the subsequent tests was obtained by leaching the NiMH powder in the following conditions: 2 stages, $[\text{H}_2\text{SO}_4] = 2 \text{ M}$, $T = 25 \pm 1^\circ\text{C}$, $\text{S/L ratio} = 1/10 \text{ g ml}^{-1}$ and $t = 2 \text{ h}$. The solutions were mixed and filtered to remove solids in suspension. As the pH of the leach solution was near zero, NaOH was added to raise the pH to 2.5. Consequently, the formation of a dense and white precipitate was verified. The solution was filtered again and the solid phase was dried and stored. The precipitation still lasted for some days but at a very slow rate; then, the solution was filtered for the

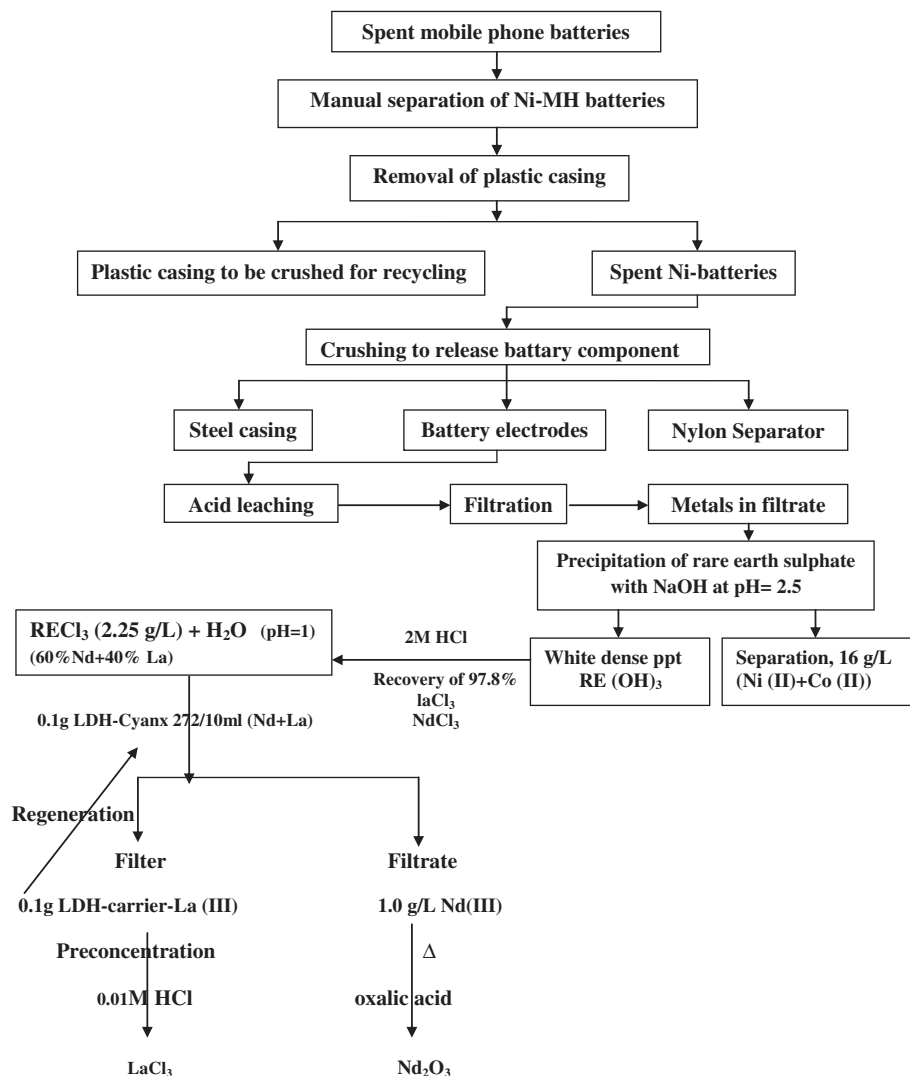
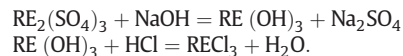


Fig. 12. Overall flowsheet for separation and recovery of Nd(III) and La(III) from spent Ni-MH batteries.

third time. Samples of the final solution were analyzed by AAS for Co and Ni while samples of the precipitate were submitted to EDX analysis Fig. 11.

The rare earth sulfate deposited in the leaching process was transformed into rare earth hydroxide. High concentrated HCl remaining in the back-extract could neutralize rare earth hydroxide to form rare earth chloride. The reaction is:



The rare earth chloride was concentrated and crystallized to form crystalline rare earth chloride. The overall recovery of rare earths was about 98.5%.

3.7. Recovery of La(III) and Nd(III) from NiMH battery

Based on the results obtained, a flow sheet for separation of La(III) and Nd(III) from white dense precipitate ($\text{RE}(\text{OH})_3$) was developed and tested. In this concern, synthetic adsorbent has been used for separation of La(III) and Nd(III) from leaching solution. After leaching one cell of the batteries electrodes by 2 M sulfuric acid, the resulted leaching solution was found to contain 16 g Co(II) and Ni(II) (2 g cobalt, 14 g nickel, 0.13 g iron and 2.25 g lanthanides). The adsorption process for lanthanides (La(III) and Nd(III)) from white precipitate were carried out by using 0.1 g adsorbent/10 ml solution at 25 °C for 2 h to adsorb 1.25 g La(III). Under these conditions, the solid phase was separated and the aqueous phase was analyzed. The results obtained indicated that the adsorption percentages are 98% La(III) and 1% Nd(III). Stripping of pure La(III) from the solid phase was carried out using 0.01 M HCl at 25 °C. The stripped solution contained > 1.24 g La(III) and < 0.02 g Nd(III). Nd(III) was removed from the filtrate solution as a Nd(III) oxalate precipitate by addition of 10 g oxalic acid. Then, the subsequently roasting Nd(III) oxide was obtained by the calcination solids at 500 °C for 3 h. The resulted powder obtained showed that the percentage precipitation of Nd(III) was > 97% (0.97 g) and < 0.8% (≤ 0.01 g) of La(III), Fig. 12.

4. Conclusions

- ◆ Mg–Fe–LDH–Cyanex-272 was prepared using separate nucleation and aging steps.
- ◆ The optimum conditions of the separation of 5 g/l of La(III) and 5 g/l Nd(III) were contact time = 2 h, adsorbent weight/10 ml = 0.1 g/10 ml and pH = 1 at 25 °C.
- ◆ The technical feasibility of recovering rare earths from the sulfate leachate solution obtained from NiMH spent batteries has been demonstrated by means of real solution.
- ◆ Considering the high cost of the enriched ores such as monazite sand and bastnaesite (about US\$3/kg in 1997), spent batteries can be considered as potential source of metals: from 1 t of spent batteries (all materials), 37.5 kg of RE (as metal) at about 80% of purity can be obtained, very close to the bastnaesite composition. Moreover, two important objectives can be attained: waste treatment/recycling and natural resource conservation.
- ◆ A mixture of rare earth elements can be separated from the acid leach liquor by precipitation with NaOH. In this study, a dense white precipitate was obtained thus corresponding to removal of rare earth elements.
- ◆ Leaching with sulfuric acid was considered efficient for the dissolution of metal content of NiMH battery powder. Cobalt and nickel were easily leached from the powder; around 85% of nickel and

98% of cobalt was leached from the NiMH powder in one single stage. The full extraction of nickel and rare earth elements will require staged operation nearby more than 95% of rare earth elements (La + Nd) was leached in two stage operation.

- ◆ Mg–Fe–LDH–Cyanex-272 was found to be effective for recovery of La(III) more than Nd(III). The recovery percent of La(III) and Nd(III) from the spent battery was found to be about 98%.
- ◆ The adsorption capacities of the prepared adsorbent for La(III) and Nd(III) were 481 and 192 mg/g, respectively.
- ◆ Mg–Fe–LDH–Cyanex-La(III) was leaching using 0.01 M HCl.
- ◆ The LDH-carrier is economic and efficient where the same LDH can be used for more than seven times.
- ◆ Recovery of spent NiMH batteries provides multipurpose targets; control the hazardous materials, protect the environment against pollution; conserve the mineral resources and recover pure valuable La(III), Nd(III) and chemical compounds needed in the market. The applied method is environmentally friendly with no hazardous by-products. The cost of recovered products is competitive with the market price for the same chemicals prepared from primary resources.

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